On a Method of Measuring the Viscosity of the Vapours of Volatile Liquids, with an Application to Bromine.

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(Communicated by A. W. Porter, F.R.S. Received April 22,—Read June 19, 1913.)

The determination of several of the physical properties of the halogens is rendered difficult by reason of their great chemical activity. This is particularly the case where pressure measurements are involved, it being almost impossible to choose a gauge fluid which is unacted upon by these elements. It was in order to surmount this difficulty that the following method was devised, and this paper deals with its application to the determination of the viscosity of gaseous bromine at various temperatures. It will be seen that in the apparatus used the only possibility of chemical action is between the bromine and the glass, and the author has been given to understand that this does not occur to any appreciable extent. Although originally designed for the purpose of avoiding chemical action, the method to be described appears to form a very suitable means of determining the viscosity of the vapour of any volatile liquid, the only data required being the saturation vapour pressures over a small temperature range and the densities of the liquid over the same range.

Method of Experiment.

The method is based upon O. E. Meyer's transpiration formula, and the modifications of the older methods consist in the special devices adopted for estimating the pressures at the two ends of the capillary tube, and for measuring the quantity of gas passing through it. Fig. 1 shows an ideal form of the apparatus, which will suffice to indicate the principles involved. A and B are two glass bulbs connected by a capillary tube, and the

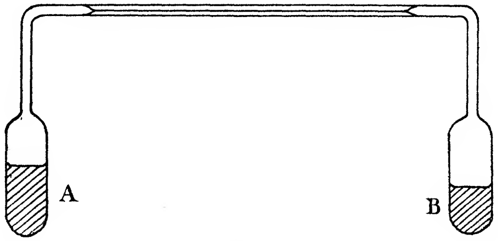

Fig. 1.

apparatus contains nothing but the liquid and its vapour. If A is maintained at a higher temperature than B, the liquid will evaporate in A and condense in B. With a capillary tube of sufficiently narrow bore it would obviously be possible to restrict the rate of flow so as to secure that the pressures in A and B were the saturation vapour pressures at the temperatures of the respective enclosures. The mass of gas traversing the capillary tube in a specified time could be estimated either from the volume of liquid disappearing from A or from that condensing in B, provided that the density of the liquid be known. All the data for measuring the viscosity of the vapour would then be available, and by maintaining the capillary tube at various temperatures higher than that of A (this to secure that no condensation should occur elsewhere than in B), the viscosities at those temperatures could be determined. Further, the apparatus being symmetrical, measurements in alternate directions could be performed successively.

In practice, however, the experiment is scarcely so simple as this. Owing to the smallness of the volume of liquid corresponding to a large volume of vapour, it is clearly desirable that the vessels A and B should not be bulbs, but should take the form of graduated tubes, narrow in bore, although not of course, comparable in this respect with the capillary itself. When this is the case it is found that with a capillary whose bore is of sufficient size to permit of accurate measurement, the pressures at the two ends are no longer equal to the saturation vapour pressures for the temperatures of the baths in which A and B are immersed. This is, of course, to be attributed to the fact that when the rate of distillation through the capillary is large, heat can neither enter A nor leave B rapidly enough to secure equilibrium between the liquid and its vapour. The consequence is that the pressure in A is less than, and that in B greater than the corresponding saturation pressures, and in order to find the true pressures means have to be adopted for estimating the above differences. A consideration of the diagram of the apparatus actually used will show how this was achieved. It will be seen (fig. 2) that the vessels A and B are U-tubes, sealed at the ends remote from the capillary. They are enclosed in water baths, the temperatures of which differ by several degrees. Let us suppose that that containing A is at the higher temperature. The temperature of the bath containing A must be lower than that of any other part of the apparatus except B, and, with this restriction, the temperature of the bath C containing the capillary tube may be maintained at the value at which it is desired to determine the viscosity of the vapour. The vapour which evaporates from A passes through the glass spiral *a* in order that it may be raised to the desired temperature before entering the capillary. After emerging from the other end it is eventually condensed to liquid in B.

Now let us consider what happens in the closed limbs of the vessels A and B. The variations of level to which the liquid is subject in these limbs is not such as to involve appreciable evaporation or condensation there; consequently the saturation pressures are maintained. In the limbs adjacent to the capillary, however, owing to rapid evaporation and condensation, the pressures differ from the saturation values, but by amounts which can be easily estimated by observing the differences of level in the two limbs of the U-tubes. Thus suppose t_1 and t_2 are the temperatures of the baths containing A and B respectively, ρ_1 and ρ_2 the densities of the liquid at these temperatures, p_1 and p_2 the pressures at the two ends of the capillary, and h_1 and h_2 the differences of levels of the liquid in the respective U-tubes, then

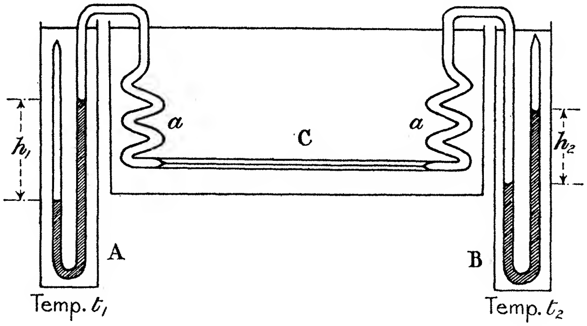

FIG. 2.

$$p_1 = (\text{saturation pressure at } t_1) - g\rho_1 h_1,$$

$$p_2 = (\text{saturation pressure at } t_2) + g\rho_2 h_2.$$

Thus, provided that the saturation vapour pressures and the liquid densities over a small temperature range are known, the pressures controlling the transpiration can be found without using anything in the nature of an ordinary pressure gauge. Further, a knowledge of the specific volumes of vapour and liquid provides means of determining the rate of flow through the capillary, from observations of the volume evaporation and condensation of the liquid.

Although the results recorded here are confined to bromine, the method will probably be found suitable for measuring the viscosity of the vapours of such elements as iodine, phosphorus, and sulphur, besides many volatile organic substances.

Experimental Details and Dimensions of Apparatus.

It happens that, in the case of bromine, a suitable pressure difference may be secured by keeping one of the **U**-tubes at the temperature of melting ice, and the other slightly below atmospheric temperature. They were therefore enclosed in deep rectangular vessels with plate glass sides, which could be filled either with a mixture of crushed ice and water or water near the temperature of the atmosphere. Both were kept thoroughly stirred by means of paddles, and by this means fairly constant temperatures were maintained. The low-temperature side remained steadily a few hundredths of a degree above 0° C., while the other side warmed so slowly—at most about $\frac{1}{2}°$ C. per hour—that it was quite justifiable to take the mean value as the effective temperature. The capillary tube and spirals were in a large copper vessel which contained water for the lower temperatures and liquid paraffin for temperatures above 100° C. By reason of the large amount of liquid present, which was kept thoroughly stirred throughout, the temperature could easily be kept practically constant by suitably adjusting the gas supply. The vessels A and B (fig. 2) were effectively shielded from C. Observations were obtained with C at six different temperatures ranging from 13° C. to 220° C. The rate of evaporation of liquid was naturally diminished by raising the temperature of the capillary, both on account of the increase of specific volume of the vapour and its increased viscosity. The adjustment was, however, not wholly effected in this manner, and it was rather surprising to find that the rate of evaporation was not greatly diminished. The explanation lies in the fact that the pressure difference between the ends of the capillary assumed a higher value; in other words, the experiment approached more nearly to the ideal case referred to in the beginning of this paper.

The **U**-tubes A and B were about 2 mm. in internal diameter, and each limb was about 20 cm. long. They were graduated in millimetres and carefully calibrated. The length of the capillary tube was about 39 cm., and the radius approximately 0·018 cm. In transpiration experiments, however, the dimension required is the effective value of l/R^4, where l is the length and R the radius of the equivalent uniform capillary. In order to allow for the conical ends and other irregularities in the tube, calibration with a short thread of mercury was used in order to determine the sum $\Sigma(\delta l/r^4)$, where δl is any short length and r the radius in that neighbourhood. The advantage of this method is that it gives proper weight to the retarding effects of the various portions of the tube, and indicates how far it is justifiable to ignore the viscous retardation in parts of the apparatus other than the capillary itself. In the apparatus in question no correction comparable with the experimental error was necessary on this account. The actual value of $\Sigma(\delta l/r^4)$ was $3\cdot763 \times 10^8$ cm.$^{-3}$.

The method of obtaining the data necessary for calculating the rate of flow of gas and the pressures at the two ends of the capillary was to take time readings of the positions of the four liquid levels—two on the evaporation side and two on the condensation side. The masses of bromine evaporating and condensing in the same given time were always found to be nearly equal, but calculations have been made from the rate of evaporation only, since there was no guarantee that the whole of the condensed vapour found its way at once into the liquid already there; in other words, the amount of liquid in the process of flowing down the walls of the condensation tube at any given instant was not necessarily constant. The readings on the condensation side were, however, necessary for the estimation of the pressure, and the average difference of level both on this side and on the evaporation side throughout an experiment were found in each case. An experiment usually lasted rather more than an hour, 12 or 14 observations of each level being taken in this time. The temperatures both in the baths A and B and in the tank C (fig. 2) were obtained by means of thermometers specially standardised for the purpose, the probable accuracy being 0·01° C. in the case of A and B, and an amount varying from 0·1° C. to 0·5° C. according to the temperature in the case of C.

The apparatus was entirely devoid of taps both in its final form and during the process of filling, absence of tap grease being regarded as necessary in order to avoid the production of impurities due to chemical action upon it by the bromine.

The bromine used was of the purest quality supplied by Kahlbaum. Some difficulty was experienced in securing that the contents of the apparatus consisted only of the liquid and its vapour. Eventually the following method of procedure was adopted with success. The apparatus was first of all evacuated as far as possible by means of a mercury pump, the latter then being sealed off, leaving charcoal tubes which could be placed in liquid air to remove final traces of permanent gas. The liquid bromine was then introduced by breaking off the end of a narrow tube placed below its surface. When a sufficient quantity had entered, the narrow tube was sealed off. With the charcoal tubes now in liquid air, a portion of the bromine was allowed to evaporate so as to rid it of gases which might be dissolved in it, and finally the charcoal tubes were sealed off, and the liquid distilled into the **U**-tube A. It was noticed that, even after this procedure, a small quantity of permanent gas had survived; indeed circumstances at this stage seemed to indicate that the bromine vapour exercised a displacing action upon other gases condensed in the charcoal, and it was only by making use of a series of separate charcoal tubes that the impurity was reduced to an amount which would not seriously affect the measurement. Although a small admixture of foreign gas would not greatly alter the viscosity, it was important to remove any trace of it from the closed limbs of the U-tubes, otherwise the pressures at these points would not have the estimated values, namely, the saturation pressures of the bromine. This was done by successive condensation and evaporation of the bromine in the U-tubes, and that the process had been successful was evident from the fact that afterwards, if the closed limbs were cooled, they would become completely filled with liquid.

Calculation of Results.

Meyer's transpiration formula, upon which the present method of measurement is based, is

$$\eta = \frac{\pi R^4}{16 l} \cdot \frac{(p_1^2 - p_2^2)t}{p_1 v_1},$$

where η is the viscosity, R the radius and l the length of the capillary tube, t the time during which a volume v_1 enters the tube, and p_1 and p_2 the respective pressures at the ends where inflow and outflow occur.

This formula is developed upon the assumption that the gas in question obeys Boyle's law. It is quite possible, therefore, that if we are dealing with a gas which is only slightly superheated, we may not be justified in using this means of finding the viscosity. Indeed, this very fact may be the cause of certain irregularities which are observed in the case where the temperature of the capillary tube is only a few degrees above that of the evaporating bromine. For lack of precise information on this question, however, there was nothing to be done but to assume the validity of the formula in all cases. The same objection possibly applies also to the assumption that Charles' law is true for the vapour in the rarefied condition in which it was used, as has been done in order to connect the volume of liquid evaporating with that of the gas entering the capillary. Both these points will be treated more fully later in the paper.

With the above assumptions we may write in the transpiration formula

$$\frac{p_1 v_1}{T_1} = \frac{p_0 v_0}{T_0},$$

where T_1 = the absolute temperature of the capillary, p_0 and T_0 being normal pressure and temperature, and v_0 the volume of gas reduced to N.T.P.

Further $$m = \rho_0 v_0,$$

where m is mass of gas traversing the capillary and ρ_0 its density at N.T.P.

Meyer's formula therefore becomes

$$\eta = \frac{\pi R^4}{16 l} \cdot \frac{(p_1^2 - p_2^2) t}{p_0 m} \cdot \rho_0 \frac{T_0}{T_1},$$

the quantities variable from one experiment to another being p_1, p_2, m, t, and T_1.

The density of bromine at N.T.P., *i.e.* ρ_0, was estimated from the value of the atomic weight, 79·96, relative to oxygen. The value obtained and used was 0·007161 grm. per cm.^{3}. As has been shown, the vapour pressure of bromine and the density of the liquid over a temperature range from 0° C. to about 16° C. were needed in order to calculate p_1 and p_2 from the experimental observations. The densities were also necessary to obtain m in terms of the volume of liquid evaporating.

For the former purpose the vapour pressures due to Ramsay and Young* were taken, and to their observations was fitted, by the method of least squares, over the small necessary temperature range a parabolic formula, so as to be able to interpolate. The values of the densities of liquid bromine at various temperatures were taken from the mutually consistent results of Pierre,† Quincke,‡ J. D. van der Plaats,§ and Andrews and Carlton.|| They range from 3·187 grm. cm.$^{-3}$ at 0° C. to 3·102 grm. cm.$^{-3}$ at 25° C.

Small corrections were also applied for the expansion of the capillary tube with temperature and for the slipping of the gas over its internal walls. The former correction amounted to about 0·5 per cent. at the highest temperature at which observations were taken; the latter, which would have been almost negligible had the gas been at atmospheric pressure, was comparatively important by reason of the fact that the average pressure in the experiments was of the order of 10 cm. of mercury only. The correction for slipping, as is well known, amounts to multiplying the original Meyer's expression by the factor $(1 + 4\lambda/R)$, R being the radius of the capillary and λ a quantity which differs little from the mean free path of the gas molecules under the conditions of the experiments. The value of λ needs to be known only approximately for correction purposes, and in the present cases a sufficiently accurate value was obtained by adopting the method used by the author in previous determinations,¶ namely, to calculate λ from the approximate value of the viscosity, using the customary formula based on the kinetic theory.

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* Ramsay and Young, 'Chem. Soc. Journ.,' 1886, vol. 49, p. 453.

† Pierre, 1848.
‡ Quincke, 1868.
§ J. D. van der Plaats, 1886.
|| Andrews and Carlton, 1907.
These values were obtained from Landolt and Börnstein's tables.

¶ 'Roy. Soc. Proc.,' 1910, A, vol. 83, p. 517.

More accurate values of λ can, if required, be subsequently obtained by the method of repeated substitution. Owing to the rarefied condition of the gas in the present measurements, λ had considerably greater values than under normal circumstances, consequently the corrections on account of slipping were correspondingly greater, amounting to from 0·5 to 2 per cent., according to the temperature.

Although evidence will be given later to show that very probably bromine vapour obeys Maxwell's law, viz., that the viscosity of a gas is, over a large range, independent of the pressure, it has been thought desirable to record the values of p_1 and p_2 and their mean value. These are given (in centimetres of mercury) in Columns 2, 3, and 4 of Table I, where the results of all the experiments are tabulated. The rates of transpiration, *i.e.* the number of grammes of vapour traversing the capillary per second, are also given in Column 5. It may be mentioned, in this connection, that calculations were made to see whether an appreciable reduction in driving pressure was brought about by the velocity of transpiration of the vapour, but the amount was found to be much below the probable accuracy of the measurements.

Table I.

Temperature (absolute).	p_1.	p_2.	Mean pressure.	Transpiration rate in gr.-sec.$^{-1}$ × 10^4.	Viscosity in C.G.S. units × 10^4.
285	9·17	7·70	8·44	1·041	1·509
284·6	9·57	7·59	8·58	1·425	1·508
286·8	10·25	7·58	8·92	1·957	1·525
287·1	9·15	7·57	8·36	1·103	1·504
338·7	10·48	7·50	8·99	1·669	1·718
339	10·42	7·57	9·00	1·592	1·707
338·6	10·52	7·52	9·02	1·706	1·691
372·8	10·12	7·55	8·84	1·181	1·868
372·9	10·35	7·57	8·96	1·284	1·888
372·6	10·58	7·53	9·06	1·413	1·898
413·7	12·05	7·73	9·89	1·802	2·086
413	11·32	7·74	9·53	1·448	2·066
412·8	11·65	7·73	9·69	1·597	2·086
452·8	11·18	7·97	9·58	1·099	2·247
452·7	11·35	8·06	9·70	1·124	2·280
452·9	11·48	8·01	9·75	1·186	2·293
493·5	11·81	8·34	10·07	1·045	2·468
493·3	12·54	8·31	10·42	1·307	2·492

It will be noticed that, in each of the groups indicated above, the temperatures are approximately the same, and that the variations in values of the viscosity in any group amount to about 1 per cent. This, indeed, represents very nearly the degree of accuracy which could be expected from the particular form of apparatus used.

In Table II there are collected the mean values deduced from the previous table, and the same data are shown graphically in fig. 3.

Table II.

Temperature (absolute).	Viscosity in C.G.S. units × 10^4.
285·9	1·511
338·8	1·705
372·8	1·885
412·8	2·079
452·8	2·273
493·4	2·480

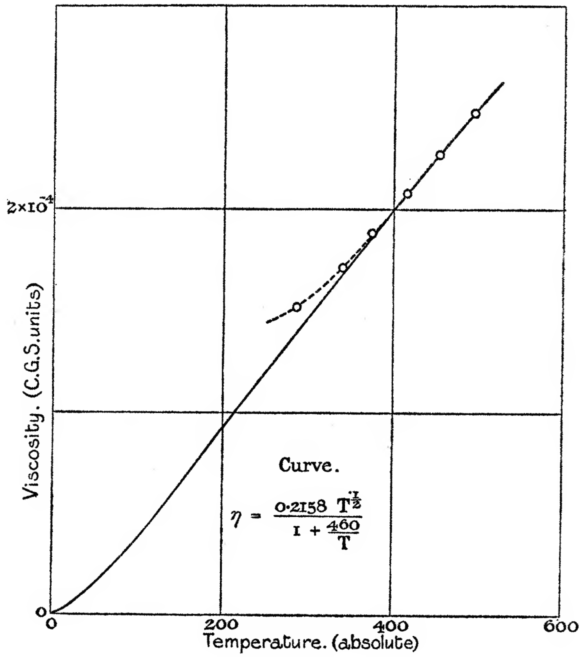

FIG. 3.

In view of the number of separate observations taken at the various temperatures, the probable error is considerably less than 1 per cent.

Discussion of Results.

There are several points of interest in connection with the results which have been obtained. In the first place, it is possible to compare one of the present determinations with a corresponding determination previously obtained by the author by a different method.* In that case the viscosity of bromine vapour was measured at 98·7° C. and atmospheric pressure. The value obtained was $1{\cdot}869 \times 10^{-4}$ C.G.S. units, and in the present case, at a pressure of about 9 cm. of mercury and a temperature of 372·8° abs., *i.e.* 99·8° C., the viscosity is found to be $1{\cdot}885 \times 10^{-4}$ C.G.S. If we interpolate so as to make the temperatures of the two values under comparison identical, the result obtained is $1{\cdot}879 \times 10^{-4}$ at 98·7° C. This is only about ½ per cent. different from the value measured by means of the earlier and entirely different apparatus and method. It seems justifiable, therefore, to conclude that the viscosity of this vapour is independent of the pressure, at any rate, through the range from 9 to 76 cm. of mercury, notwithstanding the fact that it may be only comparatively slightly superheated. It is worthy of notice also that the accordance of these two results suggests that within the degree of accuracy attained in these viscosity measurements it is probable that Boyle's law is valid, and its use in the calculation of these results permissible, at and above the temperature in question.

When we come to consider the mode of variation of the viscosity with temperature, we are met with the, at first sight, surprising result that the viscosity increases more and more rapidly as the temperature rises (fig. 3). The experimental points lie on a curve which is at first concave upwards and becomes practically straight at the higher temperatures. As far as the author is aware, no previous viscosity determinations with any gas have indicated this type of variation with temperature. No gas even approximately obeys the law deduced from the simple kinetic theory over the temperature range which has up to the present been treated experimentally; but the departures from this law hitherto observed have not been sufficiently great to alter the sign of the curvature of the theoretical curve. Ultimately, no doubt, at exceedingly high temperatures the viscosity of every gas would be proportional to the square root of the absolute temperature, but the present measurements show that at comparatively low temperatures the departures from this law are great enough to produce an actual inflexion in the curve connecting viscosity with temperature. In this connection it is interesting to observe that the equation which Sutherland proposed does show such an inflexion. The curvature of his curve $\eta = \kappa \mathrm{T}^{\frac{1}{2}}/(1+\mathrm{C}/\mathrm{T})$ (κ and C being constants) changes sign at $\mathrm{T} = (2\sqrt{3}-3)\,\mathrm{C}$ or $0{\cdot}464\,\mathrm{C}$. This has, the author believes, not been called attention to previously, probably because no such variation has been found experimentally. For nitrogen, for instance, the value of C which has been found is 113, and assuming Sutherland's equation to be valid at such temperatures, measurements of the viscosity at 52° absolute would be necessary to reach the point of inflexion, and at still lower temperatures to indicate the upward curvature. In this region the nitrogen would be normally liquid; indeed, speaking generally, all gases are so at the absolute temperature 0·464 × C, so that from this point of view experiments with the vapour at low pressures would be required to indicate this type of variation.

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* 'Roy. Soc. Proc.,' 1912 A, vol. 86, p. 166.

This is, in fact, what has been done in the present case, and although it turns out, upon closer consideration, that the correspondence, from other standpoints, between the experimental results for bromine and Sutherland's equation is by no means close, yet the very fact that the inflexion of the curve appears both practically and theoretically seems to favour the view that the modifications of the simple kinetic theory introduced by Sutherland are upon the right lines. However, the attempt to fit Sutherland's equation to the experimental points as they stand is unsuccessful. The equation involves that at absolute zero the slope of the curve is zero, and a reference to fig. 3 will show that the positions of the points are not such that a continuation of the curve through them would satisfy this condition. If, however, the two lowest temperatures are omitted from the calculation, very good agreement with Sutherland's equation is shown by the remaining four. The full curve in fig. 3 represents the equation fitted to the upper four points, and it has been continued down to absolute zero, both to show the divergence for the lower points and the point of inflexion previously referred to. In the following table (Table III) are given the observed values of the viscosity and the values calculated according to the equation

$$\eta = \frac{0{\cdot}2158\,\mathrm{T}^{\frac{1}{2}}}{1+460/\mathrm{T}} \times 10^{-4}.$$

Table III.

Temperature (absolute).	Viscosity × 10⁴.		Difference, per cent.
	Observed.	Calculated.	
493·4	2·480	2·481	−0·0
452·8	2·273	2·278	−0·2
412·8	2·079	2·074	+0·2
372·8	1·885	1·866	+1·0
338·8	1·705	1·685	+1·2
285·9	1·511	1·399	+6·2

There is obviously more probability that the equation of Sutherland will approximate more closely to the facts at higher than at lower temperature. Indeed he made no claim that it would be valid where the gas was only slightly superheated. The changes necessary to be made in the gas theory must apparently be such as will retain and at the same time raise the point of inflexion.

An alternative explanation of the divergence from the theoretical curve of the lowest point in particular is that in the observations upon which this value is based the vapour was so slightly superheated (a few degrees only), and that consequently it could not be treated as a perfect gas in the calculation of the viscosity. It seems unlikely, however, considering the fact that the pressure was so low, that an error so large as 6 per cent. would be introduced on this account.

One other point, perhaps, also deserves mention. No data are available to show what degree (if any) of association exists in the bromine vapour under the circumstances of the experiments. Obviously this might have an important effect, particularly if, as is almost certain, dissociation occurred with rise in temperature. The agreement between the values at 98·7° C., but at considerably different pressures, previously referred to is distinctly against the occurrence of appreciable association, at any rate, at that temperature.

These considerations only apply to the lower temperatures, and we may take it that at the higher temperatures Sutherland's law fits in with the facts to a considerable degree of accuracy. It is possible, therefore, to test the agreement or otherwise of the data presented in this paper with the two laws in connection with gaseous viscosities which the author has previously shown to apply in other cases.*

The first of these is that, for a large number of gases, Sutherland's constant C is proportional to the critical temperature, the relation being expressed by the equation

$$T_c/C = 1·14.$$

The critical temperature of bromine, according to Nadejdine, is 575° absolute, and the above ratio has the value $575/460 = 1·25$. This ratio is distinctly higher than 1·14, and in this respect bromine is similar to chlorine, the ratio for which is 1·28.† It appears, therefore, that although various gases without distinction of kind obey this law approximately, still better agreement is obtained when the application is confined to a single group in the periodic system.

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* 'Roy. Soc. Proc.,' 1910, A, vol. 84, p. 190; 'Phil. Mag.,' January, 1911, p. 47.

† 'Roy. Soc. Proc.,' 1912, A, vol. 86, p. 166.

The second law may be stated as follows:—For the group of inert gases the square of the viscosity at the critical temperature is proportional to the atomic weight, or

$$\eta_c^2/\mathrm{A} = \text{constant} = 3{\cdot}93 \times 10^{-10}.$$

In this numerical value η_c is in C.G.S. units and A is the atomic weight relative to oxygen. It should be pointed out that η_c is not the viscosity in the critical state, but merely the viscosity at the critical temperature, when the pressure has such values that the viscosity is independent of it. Using the values of the viscosity of bromine given in this paper, and those for chlorine communicated in a previous paper, it is possible without violent extrapolation (some 47° C. in the case of chlorine, and 82° C. in the case of bromine) to obtain by means of Sutherland's equation the viscosities at the critical temperatures.

These values are based upon Knietsch's determination (419° abs.) for the critical temperature of chlorine, and Nadejdine's determination (575° abs.) for bromine. Applying these estimates to the test under consideration the results are as follows:—

Table IV.

Gas.	Viscosity at critical temperature. η_c (C.G.S. units).	η_c^2/A.
Chlorine	$1{\cdot}897 \times 10^{-4}$	$1{\cdot}02 \times 10^{-9}$
Bromine	$2{\cdot}874 \times 10^{-4}$	$1{\cdot}03 \times 10^{-9}$

It will be at once seen that the numbers in the last column are practically identical, although not at all the same number as that for the inert gases. This suggests the possibility of the law in question being of wider application than merely to the inert gases, with the restriction that the constant of proportion is not universal, but has values peculiar to each group in the periodic table.

Finally, the values of the viscosity have been used to estimate the molecular dimensions of the two gases. For this purpose the number of molecules per cubic centimetre at N.T.P. has been taken as $2{\cdot}75 \times 10^{19}$, and Sutherland's correction arising from the intermolecular attractions has been applied. The molecular diameters and volumes are both recorded in Table V.

Table V.

Gas.	Molecular diameter (in cm. × 10^8).	Molecular volume (in cm.^{3} × 10^{22}).
Chlorine	3·15	1·30
Bromine	3·36	1·59

Apparently the dimensions of the molecules do not differ to any great extent, and this, of course, involves that the density of the atom of bromine is something like twice as great as that of chlorine.

The Hall Effect in Liquid Electrolytes.

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(Communicated by Sir J. J. Thomson, O.M., F.R.S. Received May 8,—Read June 19, 1913.)

Introduction.

The distortion of the lines of flow of an electric current in a thin metal plate by the action of a magnetic field was discovered in 1879.* Hall attributed this to the action of the magnetic field on the molecular currents in the metal film, which were deflected to one side or the other and accompanied by a corresponding twist of the equipotential lines. This explanation did not pass without criticism, and another theory of the effect found by Hall was published in 1884.† In that paper the author seeks to explain the effect by assuming a combination of certain mechanical strains and Peltier effects, a thermo-electric current being set up between the strained and the unstrained portions. The effect of such strain was to produce a reverse effect in some metals, and these were precisely the metals for which the Hall effect was found to reverse. Aluminium was the only exception.‡

In other respects, however, as shown by Hall in a later paper,§ Bidwell's

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* E. H. Hall, 'Amer. Journ. Math.,' vol. 2, p. 287; 'Phil. Mag.,' 1880, vol. 9, p. 225.

† S. Bidwell, 'Roy. Soc. Proc.,' 1884, vol. 36, p. 341.

‡ 'Nature,' vol. 29, p. 514; 'Chem. News,' vol. 49, p. 147.

§ 'Science,' vol. 3, p. 387; 'Phil. Mag.,' 1885, vol. 19, p. 419.